

# Electrochemical Analysis of Actinides in Molten Salts

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# Outline

- Significance of quantitative measurements of actinides in molten salts
- Overview of advantages and requirements of using electrochemical techniques
- Determination of required parameters
- Using electrochemical techniques for making quantitative measurements at higher actinide concentrations
  - Experimental challenges
  - Required corrections of the method
- Advantages of using AC Voltammetry
- Challenges of multicomponent systems
  - Development of new analysis method
  - Comparison of electroanalytical results with ICP-AES analysis
- Conclusions



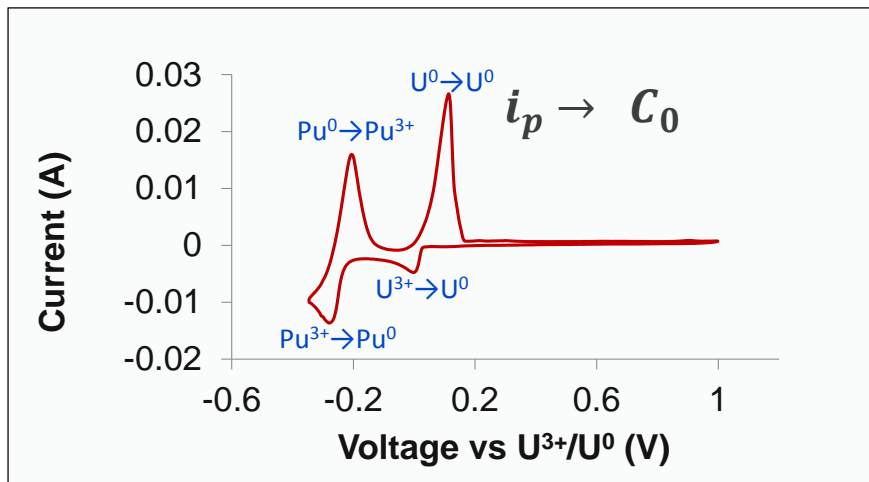
# Quantitative Analysis of Actinides in Molten Salts

Real time measurements of actinide concentrations in electrochemical recycle process are necessary for operating a commercial fuel treatment facility

- ❑ Safeguards
- ❑ Material control and accountancy
- ❑ Process control

**Electrochemical techniques are well-suited for in-situ process monitoring**

- ❑ Allow rapid, real-time measurements
- ❑ Equipment not affected by high radiation background
- ❑ Compatible with remote handling operations
- ❑ Do not require use of standards
- ❑ No sample losses during analysis



Proportionality between current response and concentration of the electro-active species constitutes the **basis of electrochemical analysis**

# Requirements for Quantitative Electroanalytical Measurements

## Accurate $i_p$ measurements

### ☐ Reproducibility

- Pre-treatment protocol to ensure reproducible electrode/electrolyte interface before each measurement

### ☐ Stability

- Non-interfering counter-reaction
- Stable reference electrode

Direct proportionality between measured peak current  $i_p$  and concentration  $C_0$

### Berzins-Delahay Equation

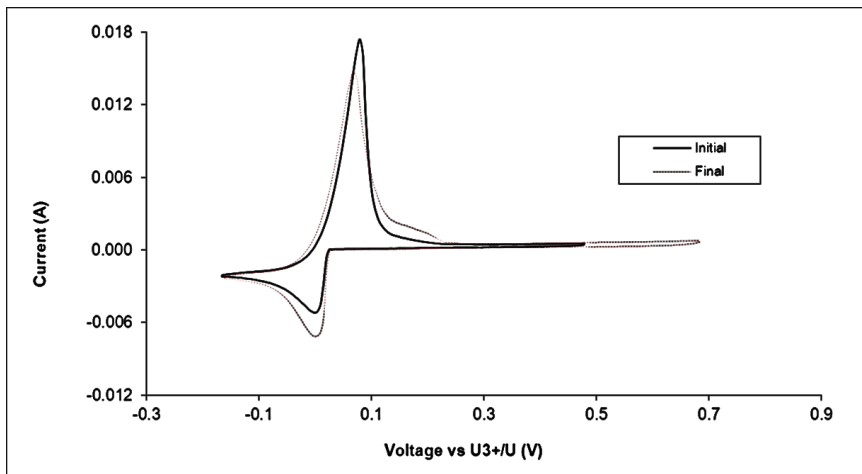
- insoluble product

$$i_p = 3.54A C_0 \sqrt{F^3 n^3 D v / RT}$$

Variable parameters :

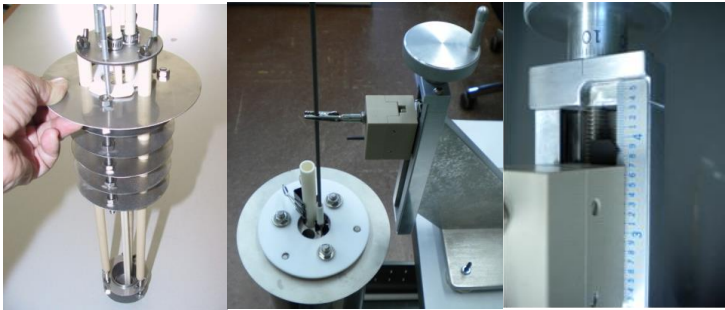
- ☐ Number of electrons transferred
- ☐ Temperature
- ☐ Area of the electrode
- ☐ Scan rate
- ☐ Diffusion coefficient

For  $C_0$  measurements all variables must be well-known and/or controllable

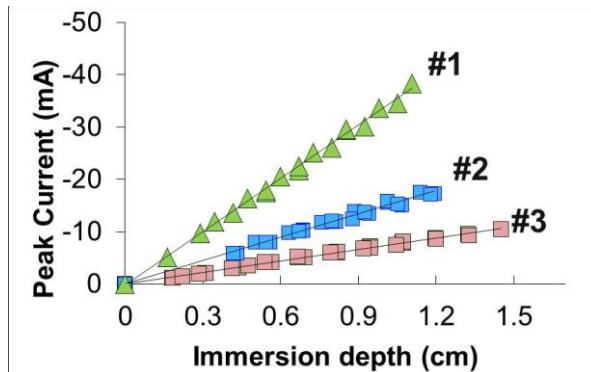


# Defining Parameters

- Area of the electrode – standard addition approach



$$\frac{di_p}{dh} = 7.08rC_0\sqrt{F^3n^3Dv/RT}$$

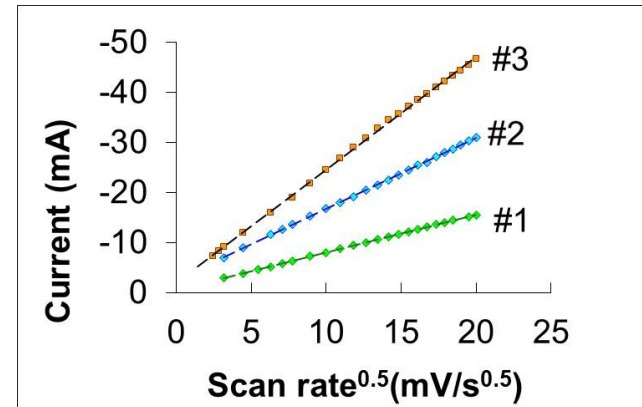


- Diffusion coefficient

- Assumed to be constant ( $1.5 \times 10^{-05} \text{cm}^2/\text{s}$  at 500degC)

- Scan rate dependence

- Linearity of  $i_p$  with  $\sqrt{v}$
  - Controls the limits of the reaction reversibility



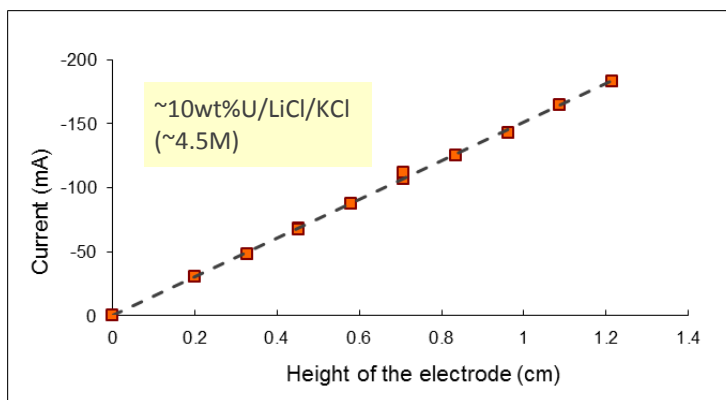
Results obtained for a SINGLE component, relatively LOW concentration salt (<1.7wt%)

Composition #	Species	ICP-AES	Voltammetry	% Error
1	U <sup>3+</sup>	0.46±0.05	0.452±0.003	0.65
2	U <sup>3+</sup>	--	0.907±0.009	0.94
3	U <sup>3+</sup>	1.73±0.17	1.767±0.003	1.5
4	Pu <sup>3+</sup>	1.33±0.13	1.336±0.001	0.97

Very good agreement between electrochemical and analytical  $C_0$  measurements

# Salts with Higher Actinide Concentrations

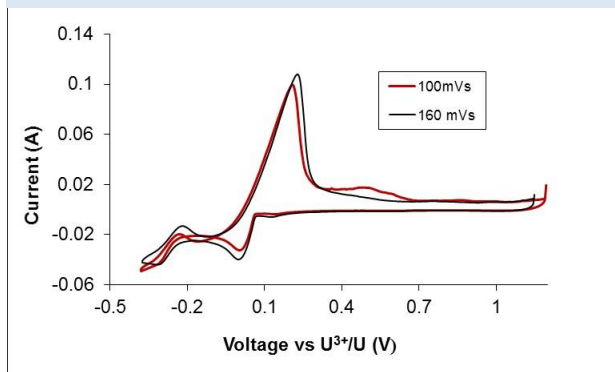
- Reproducibility is more challenging to achieve at high concentrations
  - Higher background currents and more significant area increase
  - Longer and more extensive cleaning protocol required
- Presence of unusual not peak-shaped voltammograms
  - No depletion effect at high concentrations
  - Mass transfer **is not RDS** (rate determining step)
    - Inconsistent with assumptions of Delahay equation



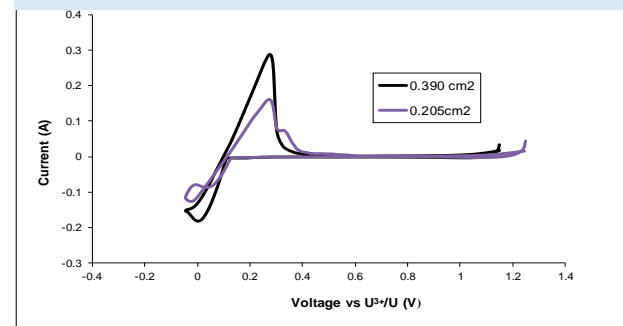
➤ Linear and reproducible plots of  $i_p$  with  $A$  and  $\nu^{0.5}$  achieved by applying proper cleaning pre-protocol and adjusting controllable parameters

## Methods to ensure mass transport limitations:

### Effect of Scan Rate Increase (~5wt%U, 1.3wt%Pu/LiCl/KCl)



### Effect of Area Increase (~10wt%U/LiCl/KCl)



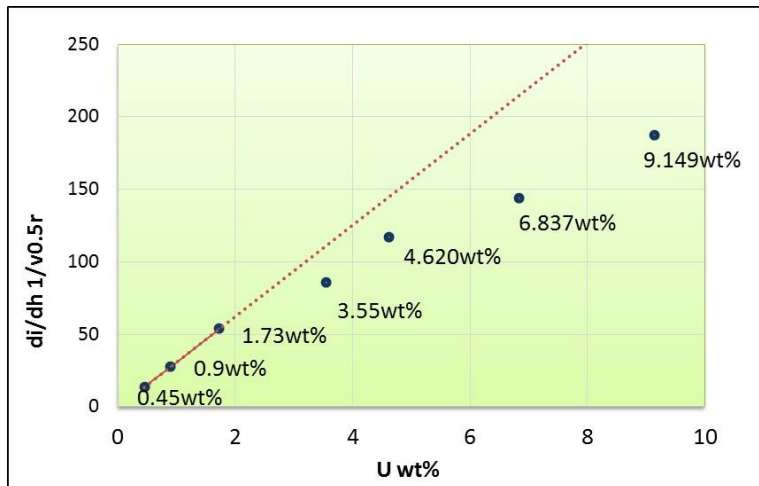
# Deviations from Linearity at Higher Actinide Concentrations

## Value of diffusion coefficient

- ☐ Can not be adjusted and/or controlled.
- ☐ Is a function of temperature
- ☐ Does it change with concentration?

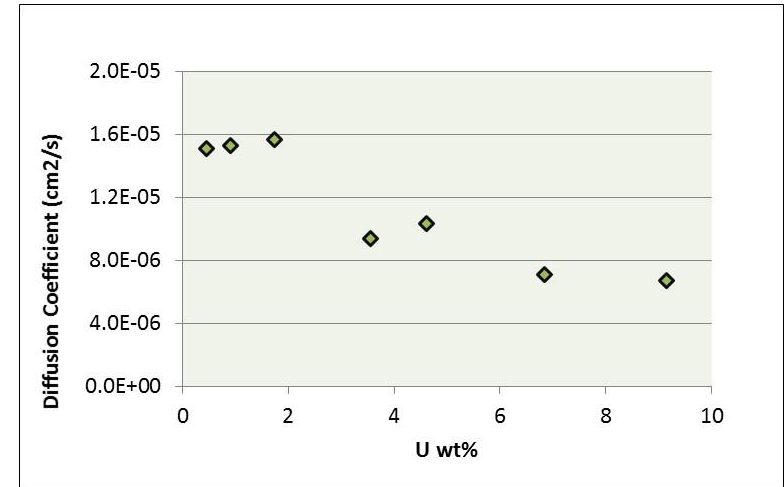
$$\frac{dl_p}{d(hrv^{0.5})} = 7.08rC_0\sqrt{F^3n^3D/RT}$$

➤ Should generate linear plot if  $D(C_0) = D$



**Deviation from linearity for U concentrations higher than ~2wt%**

Diffusion coefficient can be assumed constant only over a small change in the concentration



- ☐  $D$  decreases with increasing concentration of the diffusing species
- ☐ Can also change with other variations of the salt composition e.g. concentrations of fission products in the molten salt

U wt%	D (cm²/s)
0.45	1.51E-05
0.9	1.52E-05
1.73	1.57E-05
3.55	9.40E-06
4.62	1.07E-05
6.837	7.67E-06
9.149	6.70E-06

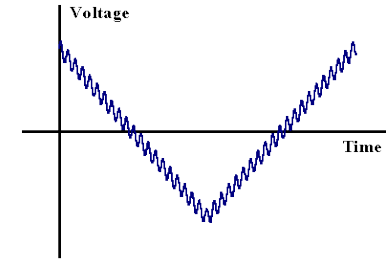
**Ability to measure/determine  $D$  INDEPENDENTLY of  $C_0$  is a crucial requirement for making real-time concentration measurements**

# AC Voltammetry for Diffusion Coefficient Measurements

- Inputs:
  - Mean dc potential ( $E_{dc}$ ) is applied linearly on a long time scale compared to that of the superimposed ac variations ( $E_{ac}$ )
- Outputs:
  - Plot of the magnitude of ac component of the current vs.  $E_{dc}$
  - Phase angle ( $\varphi$ )** between the alternating current and  $E_{ac}$

$$\varphi = \varphi(D, \omega, k_o, \alpha)$$

➤ Its value **DOES NOT** depend on concentration!!



This technique is currently being investigated:

- Theoretical derivations
- Experimentation

Any change in diffusion coefficient caused by change in concentration, and/or any other change in salt composition would be directly recorded and measured with the change in the phase angle

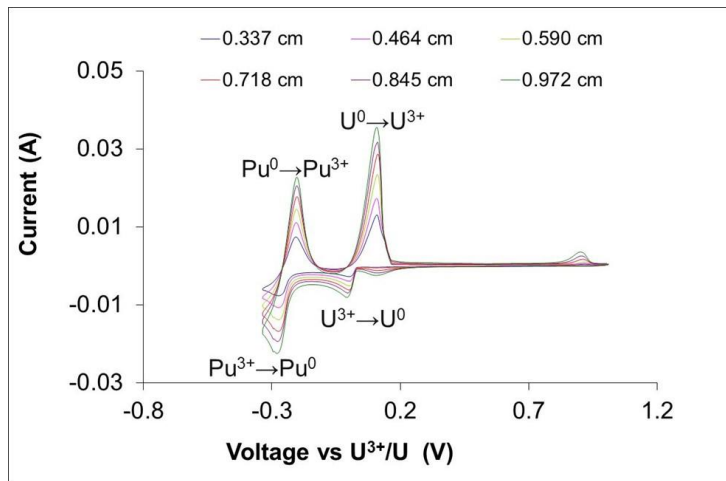
Additional advantages:

- $\varphi$  is also **area independent**
  - Very beneficial especially for a system involving an insoluble product
- Direct method to obtain kinetic parameters



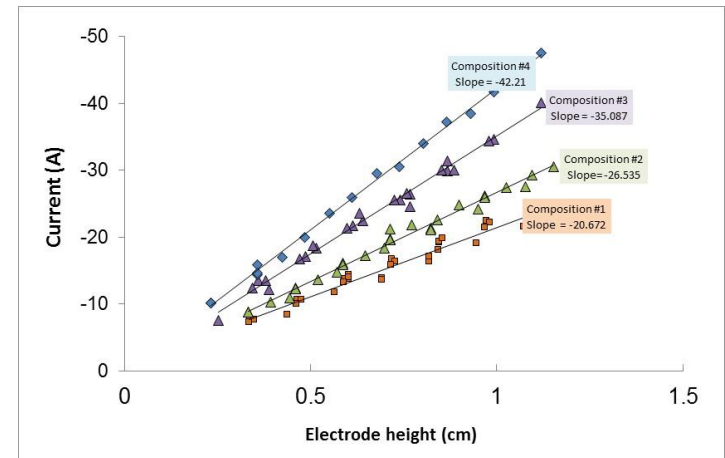
# Obtaining a Baseline for Multicomponent System

- Accurate peak height ( $i_p$ ) measurements require a reliable baseline from which to measure the peak heights
- Determination of the baseline for the  $U^{3+}/U^0$  peak is straightforward and reliable because it is the first peak in the series
- The baseline for the  $Pu^{3+}/Pu^0$  reduction peak is affected by the tail from the  $U^{3+}/U^0$  peak.



Compositions # 1-4: the same  $Pu^{3+}$  concentration, different amounts of  $U^{3+}$

→ Pu slope should remain constant



Pu slope changes significantly with increasing U concentration

Composition	Actual U wt%	Actual Pu wt%	Electroanalytical (CV) Pu wt%
1	0.45	<b>1.42</b>	<b>1.27</b>
2	1.00	<b>1.31</b>	<b>1.63</b>
3	1.99	<b>1.28</b>	<b>2.16</b>
4	4.35	<b>1.24</b>	<b>3.08</b>

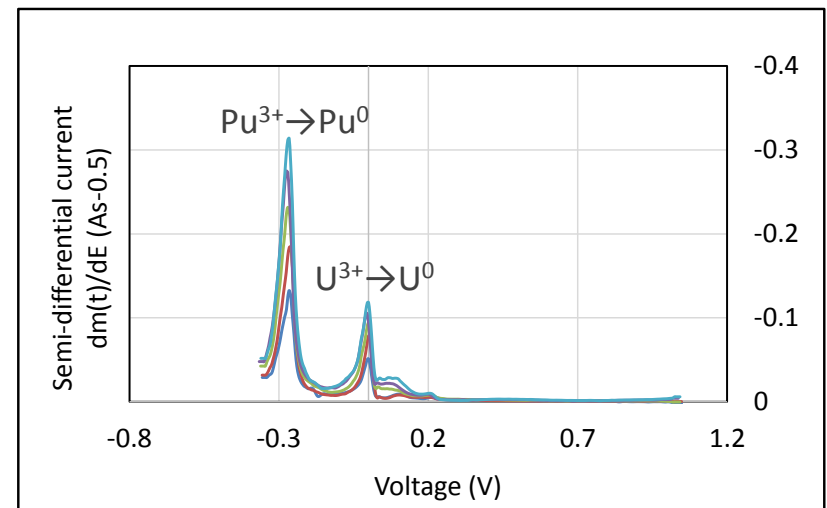
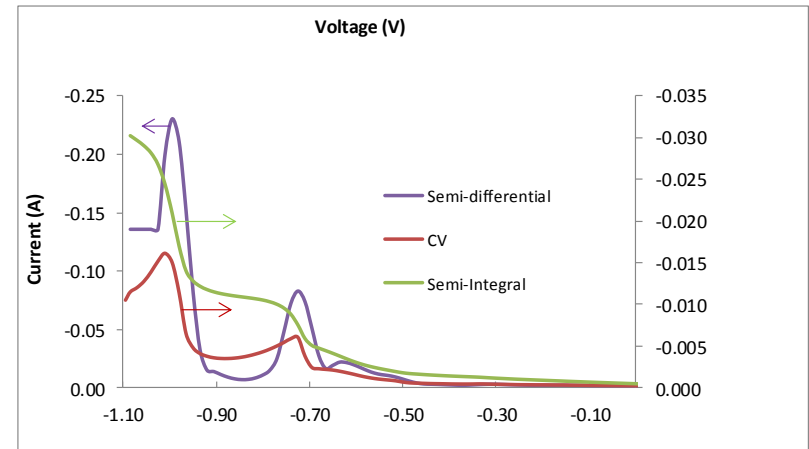
→ Need a method with better baseline resolution between peaks for concentration determination

# Semi-differential Analysis Method

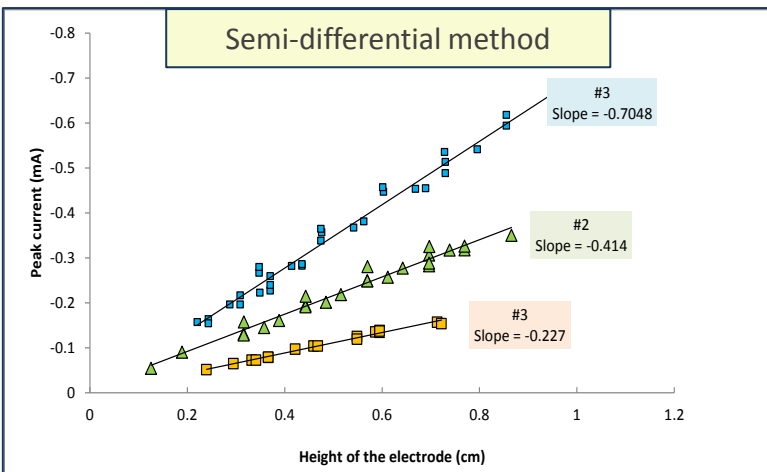
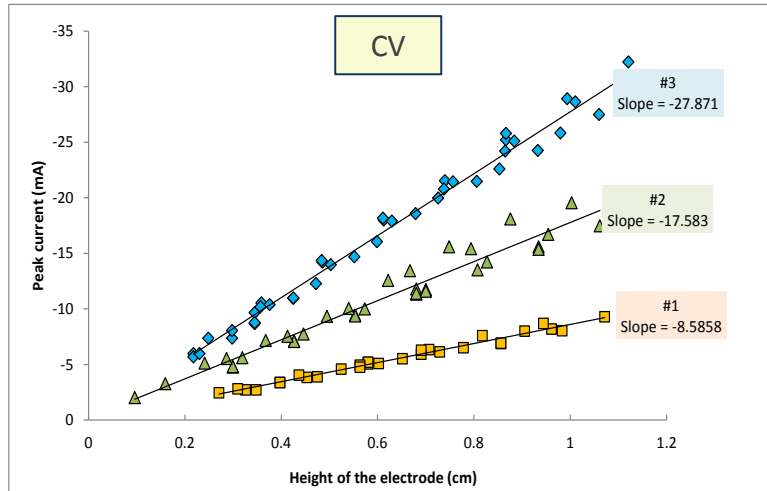
- Different method of analyzing CV data
- Generated by semi-differentiation of the current vs. time data

$$m(t) = \frac{d^{-0.5}}{dt^{-0.5}} i(t) \quad e_p(t) = \frac{dm(t)}{dt}$$

- Increases the peak height/width ratio
- Provides a better baseline for the  $\text{Pu}^{3+}/\text{Pu}^0$  peak
- Has the advantages of high sensitivity and high resolvability for the species
- Well-developed theory for soluble/soluble red-ox reactions
- Equations describing semi-differential peak for soluble/insoluble couples had to be derived



# Derivation of the Equations for Implementation of Semi-differential Method



- Nernst Equation in terms of semi-integral of current  $m(t)$  and limiting value of  $m_c$  for soluble-insoluble couple

$$E = E_{1/2} + \frac{RT}{nF} \ln \left\{ \frac{m_c - m(t)}{m_c/2} \right\}$$

- $e_p$  obtained by differentiating  $\frac{dm}{dE}$

$$e_p = \frac{C_0 n^2 F^2 A D^{0.5}}{2RT}$$

$$\frac{de_p}{dh} = \frac{C_0 n^2 F^2 r \pi D^{0.5}}{RT}$$

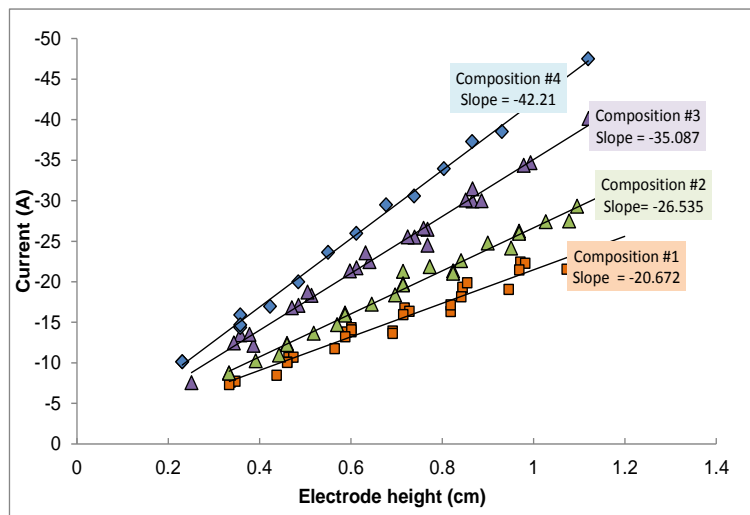
- Derived equations have been verified using U data by comparing values calculated using CV (Delahay equation) and semi-differential method

Concentration of  $U^{3+}$

Composition	U wt% Actual	U wt% CV	U wt% Semi-differential
1	0.45±0.05	0.52±0.01	0.558±0.003
2	1.00	1.06±0.03	1.017±0.006
3	1.99	1.68±0.05	1.731±0.005

# Remarkable Accuracy of $\text{U}^{3+}$ and $\text{Pu}^{3+}$ Measurements

Composition	Species	wt% ICP-AES*	wt% CV	wt% Semi-differential
1	U	0.45±0.05	0.52±0.01	0.558±0.003
1	Pu	1.42±0.14	1.27±0.03	1.37±0.01
2	U	1.00	1.06±0.03	1.017±0.006
2	Pu	1.31±0.13	1.63±0.03	1.46±0.01
3	U	1.99	1.68±0.05	1.731±0.005
3	Pu	1.22±0.12	2.15±0.04	1.264±0.008
4	Pu	1.44±0.14	3.08±0.02	1.445±0.007



Semi-differential concentration measurements of both  $\text{U}^{3+}$  and  $\text{Pu}^{3+}$  are in excellent agreement with the ICP-AES concentration measurements with extremely small relative error

# Concluding Remarks

- Voltammetry is a tool for *in situ* process monitoring of electrochemical process operations
- Very good agreement between electrochemical concentration measurements and ICP-AES sample analysis for a single component, relatively low concentrated salts
- Voltammetry at higher concentrations:
  - Additional electrode pre-treatment procedures and adjustments necessary to obtain reproducible results
  - Diffusion coefficient changes with increasing concentrations
  - Deviations from linearity for U concentrations higher than 2wt%
- Application of AC Voltammetry for diffusion coefficient measurements
  - Can be used for independent diffusion coefficient measurements
  - Enables determination of kinetic parameters
- New method for analyzing CV data was developed to eliminate concerns with baseline identification
- Semi-differential concentration measurements of both  $\text{U}^{3+}$  and  $\text{Pu}^{3+}$  are in excellent agreement with the ICP-AES concentration measurements with extremely small relative error



# Acknowledgements

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